

6. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting and/or measuring and monitoring boron in environmental media and in biological samples. The intent is not to provide an exhaustive list of analytical methods that could be used to detect and quantify boron. Rather, the intention is to identify well-established methods that are used as the standard methods of analysis. Many of the analytical methods used to detect boron in environmental samples are the methods approved by federal agencies such as EPA and the National Institute for Occupational Safety and Health (NIOSH). Other methods presented in this chapter are those that are approved by groups such as the Association of Official Analytical Chemists (AOAC) and the American Public Health Association (APHA). Additionally, analytical methods are included that refine previously used methods to obtain lower detection limits, and/or to improve accuracy and precision.

6.1 BIOLOGICAL MATERIALS

Methods for the determination of boron in samples of toxicological interest have been summarized (Stokinger 1981; Van Ormer 1975). Usually total boron is determined, although in limited cases specific boron species can be determined as well. Boron is very poorly measured by atomic absorption analysis. High-temperature atomic spectrometric methods, especially inductively coupled plasma atomic emission spectrometry, including atomic emission spectrography, work well for boron. Colorimetry and prompt neutron activation analysis can also be used.

Methods for the determination of boron in biological materials are summarized in Table 6-1.

Normally, for determination in biological samples, the sample is digested or ashed, and the boron is measured by atomic spectrometric determination.

6.2 ENVIRONMENTAL SAMPLES

Methods for the determination of boron in environmental samples are summarized in Table 6-2.

Boron is readily measured in multielement analyses of air, water, and solid waste samples by inductively coupled plasma (ICP) atomic emission spectroscopy, the method of choice for the determination of boron in modern practice. Although not multielement procedures, calorimetric cucumin and calorimetric carmine methods are still reliable methods for the determination of boron in water, air and solid waste samples. These calorimetric procedures provide adequate methods when ICP instrumentation is not available.

TABLE 6-1. Analytical Methods for Determining Boron in Biological Materials

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Blood and urine	Ashed, dissolved in HCl	SA	5 µg/100g blood 40 µg/L urine	No data	Imbus et al. 1963
Blood	Ashed by oxygen in a Parr bomb, dissolved	Colorimetric carmine method	<0.1 µg/mL	84% at 5 µg/mL	Hill and Smith 1959
Serum (borate)	Deproteinized, allowed to react with reagent	Colorimetric carmine method	>endogenous levels which are <20 mg/L	92%-104%	Baselt 1988
Blood	Ashed, dissolved	Electrophoresis	No data	No data	Hill et al. 1957
Biological material ^a	Acid digestion	ICP/AES	5 µg/L ^b	No data	EPA 1986a

^aThis method is for water, sediments, and wastes.

^bMethod detection limit. Actual detection limits for boron in waste samples may be considerably higher.

ICP/AES = inductively coupled plasma atomic emission spectroscopy; HCl = hydrochloric acid; SA = atomic spectrographic analysis

TABLE 6-2. Analytical Methods for Determining Boron in Environmental Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Air	Collection on filter, workup in acid	ICP/AES	1 µg per sample	103% recovery	NIOSH 1984
Air for boron carbide	Collection on filter, ashed, suspended in 2-propanol, redeposited on silver membrane filter	x-ray powder diffraction	0.05 mg	No data	NIOSH 1985a
Water	Direct analysis	Colorimetric curcumin	0.2 µg	23% RSD	APHA 1985a
Water	Ash, dissolve in acid	Colorimetric carmine	2 µg	36% RSD	APHA 1985b
Water	Acidify, inject	ICP/AES	0.3 µg/L	No data	APHA 1985c
Water	Direct analysis	Colorimetric curcumin	0.2 µg	23% RSD	EPA 1983
Water	Filter, acidify	ICP/AES aspiration	5 µg/L	No data	EPA 1982
Sediments, solid wastes, sludges	Acid digestion	ICP/AES	5 µg/L ^a	No data	EPA 1986a

^aMethod detection limit. Actual detection limits for boron in waste samples may be 1-3 orders of magnitude higher.

ICP/AES = inductively coupled plasma atomic emission spectroscopy; RSD = relative standard deviation

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6.3 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of boron is available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of boron.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that, if met, would reduce or eliminate the uncertainties of human health assessment. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

6.3.1 Data Needs

Methods for Determining Biomarkers of Exposure and Effect. Boron can be determined sensitively and selectively by inductively coupled plasma atomic emission analysis (EPA 1986a; Imbus et al. 1963). This method of analysis requires that the analyte be placed in solution, which can be a problem with some of the more refractory boron species. With the exception of boron carbide (NIOSH 1985a), methods are lacking for the determination of specific boron compounds.

Methods for the determination of metabolites of boron in biological materials would be useful in studying the toxicity and metabolism of this element.

More specific methods for biomarkers of exposure would be helpful in toxicological studies of boron.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. Inductively coupled plasma atomic emission spectrometry is the only satisfactory multielement method available for the determination of boron in water, air, and solid waste samples (APHA 1985c; EPA 1982, 1986a; NIOSH 1984). Calorimetric procedures are as sensitive and precise but are more labor intensive. Calorimetric procedures do provide adequate methods for those laboratories that do not have ICP instrumentation. There is a need for methods that require less expensive instrumentation, although such methods would be very difficult to develop.

Sampling methodologies for very low level elemental substances like boron continue to pose problems such as nonrepresentative samples, insufficient sample volumes, contamination, and labor-intensive, tedious extraction and purification procedures (Green and LePape 1987).

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6.3.2 On-going Studies

Examination of the literature does not suggest that major efforts are underway for the development of better methods for the determination of boron. This is due to the difficulties inherent in determining boron and the fact that an emphasis has not been placed on developing such methods because the element is relatively nontoxic.

